A review of the existing and alternative methods for greener nitrogen fixation

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Abstract

The conversion of atmospheric nitrogen into valuable substances such as fertilisers and fine chemicals is essential for agriculture and many other processes that sustain life on the planet. Although the Haber-Bosch process is the most important method of nitrogen fixation, the process is associated with major environmental concerns because it is very energy intensive and requires non-renewable feedstock to generate hydrogen. Hence, alternative ways of nitrogen fixation are being studied, from plasma synthesis and biological processes to metallocomplex catalysis, while existing methods are being improved using novel catalysts. This review covers all of the major areas of nitrogen fixation, discusses the industrial feasibility of each process, the reaction mechanisms, and provides a comparative evaluation of the various nitrogen fixation processes in terms of energy efficiency. Considering energy efficiency, the Haber-Bosch process and non-thermal plasma nitrogen fixation are promising methods for green industrial nitrogen fixation. Although metallocomplex nitrogen fixation takes place at ambient pressures, energy estimations show that this method does not provide higher energy efficiency than biological nitrogen fixation or the Haber-Bosch process. Biological nitrogen fixation on the other hand, has energy efficiency comparable to that of the Haber-Bosch process.

Keywords: Nitrogen fixation, Haber-Bosch, Energy efficiency, Plasma, Birkeland-Eyde

1. Introduction

Nitrogen is an essential constituent of all living organisms and can be found in amino acids, proteins and nucleic acids. Animals, including humans, consume nitrogen in the form of organic compounds, requiring eight to ten particular amino acids for their nutrition. The human body requires 1-2 g of protein per kg of body mass per day to survive [1–3]. Plants and bacteria, on the other hand, are less demanding because they can synthesise the much-needed amino acids from various organic and inorganic nitrogen compounds. However, the most abundant nitrogen source, the atmosphere, is not available to the majority of organisms because of the inertness of molecular nitrogen due to the high strength of its triple bond and very stable electron configuration which make almost any first reaction step unusually energy demanding. As a result, the most challenging stage of nitrogen fixation (NF) is the conversion of dinitrogen molecules into simple nitrogen compounds such as ammonia or nitric oxide which can be further used as precursors for the synthesis or biosynthesis of more complex molecules. This problem is being addressed by active research into various methods of NF including the Haber-Bosch (H-B) process, plasma synthesis, biological NF, and metallocomplex NF.

The production of nitrogen fertilisers from atmospheric nitrogen has been a major problem at the beginning of 20^{th} century [4]. In 1913, the H-B process of the high-pressure binding of nitrogen with hydrogen was introduced providing much needed fertilisers. From then on, NF has progressed in much the same manner as the growth in human population, and nowadays, about 40% of world population depend on nitrogen fixed by the H-B process [3,5]. Recently, the amount of synthetic nitrogen obtained by human activities has exceeded natural biological fixation [6]. This intensification has

led to more than doubling of the number of humans supported by a hectare of arable land [2,4].

Extensive use of NF however, comes at a price as the H-B process consumes more than 1% of the world's total energy production, emits more than 300 million metric tons of carbon dioxide and utilizes about 2% of the world's natural gas output, which is converted to hydrogen by steam reforming process [7–9]. Therefore, there is room for efficiency optimisation in NF because even minor benefits multiplied by world-scale production will give rise to huge economic savings.

To address the environmental and other concerns associated with the H-B process, research is conducted in many areas aiming to (a) improve the catalysts for the H-B process while decreasing the reaction temperature and pressure, (b) investigate plasma methods, (c) explore the mechanism of biological NF, and (d) investigate ways of NF with metallocomplex homogeneous catalysts under ambient pressure. These methods fall into two groups. The first group uses carefully optimised catalysts to perform NF under mild conditions by a slow, stepwise process of adding one electron after another while the second group uses extreme conditions of temperature and pressure to weaken the strong dinitrogen bonds. Both methods have been demonstrated in biological metallocomplex systems and in industry respectively. This review also discusses and evaluates the various NF methods in the light of current research and compares the methods in terms of energy efficiency, environmental impact and sustainability.

2. The Haber - Bosch Process

The Haber-Bosch process represents a major success of industry. It is now the most important source of nitrogen compounds and, although ammonia synthesis is one of the most studied reactions, modern iron catalysts are essentially the same as they were a century ago [10]. The iron catalysts are promoted with oxides of aluminium and potassium. Aluminium acts mainly as a structural promoter, preventing the sintering of iron particles and has no direct effect on the reaction rate [10–12]. Potassium increases the rate of ammonia formation by more than two orders of magnitude due to a combination of electron donation leading to a weakening of the dinitrogen bond and facilitating ammonia desorption from the catalyst surface [13–16]. Iron catalysts require high temperatures (650-750K) for their operation in order to increase reaction rates and high pressure of about 100 bars to compensate for the shift in ammonia equilibrium concentration. These conditions mean high energy consumption, high equipment and gas compressions costs [9].

In the 1990s, novel carbon-supported Ru catalysts were applied industrially, capable of operating at a lower reaction pressure [9,17–19]. They are usually promoted with Cs and Ba [20,21] which, similar to alkali promoters of Fe catalysts, increase electron density on Ru nanoparticles [22,23]. An important area of continuing research is how to enhance the thermal stability of the support which can achieved by graphitisation of carbon support by thermal annealing [24] or by using alternative non-carbon supports such as $MgAl_2O_4$ [25], boron nitrite [26] or electron-trapping mixed calcium-aluminium oxide [27]. The activity of ruthenium-based catalysts is higher than that of iron catalysts, which suggests that the reaction temperature and pressure may be reduced, or

Ru catalysts may be used in combination with iron-based catalysts to increase ammonia production in a smaller reaction volume. On the other hand, Ru-based catalysts are prone to deactivation by chlorine or sulphur [28–32], and are also significantly more expensive. Recently, a novel class of catalysts was proposed – ternary nitrides including Co_3Mo_3N or Fe_3Mo_3N [33] obtained by ammonolysis from the corresponding molybdate precursors [34]. The most active Cs-promoted Co_3Mo_3N catalyst was twice as active as commercial iron-based catalyst under industrial conditions, and was resistant to deactivation for at least many weeks [33,35–38].

Ammonia synthesis is a structure sensitive reaction. On Fe catalysts, active sites are surface atoms with coordination number 7, while on Ru active sites, called B_5 step sites, are ensembles of 5 Ru atoms [25,39,40]. Ammonia synthesis using industrial catalysis is described by a dissociative mechanism involving the adsorption of dinitrogen and dihydrogen molecules on the surface of the catalyst while hydrogen molecules quickly dissociate at a temperature above 473 K, forming highly mobile adsorbed hydrogen species on the catalyst surface, Fig. 1a. Molecular nitrogen, in contrast, is weakly adsorbed and may dissociate with low probability producing atomic nitrogen species which are bound strongly to the catalyst surface, Fig. 1b. Adsorbed hydrogen species react with adsorbed nitrogen to form ammonia, followed by desorption from the catalyst surface, Fig. 1c [11,41,42]. The rate-limiting step is dissociation of dinitrogen under all industrial conditions.

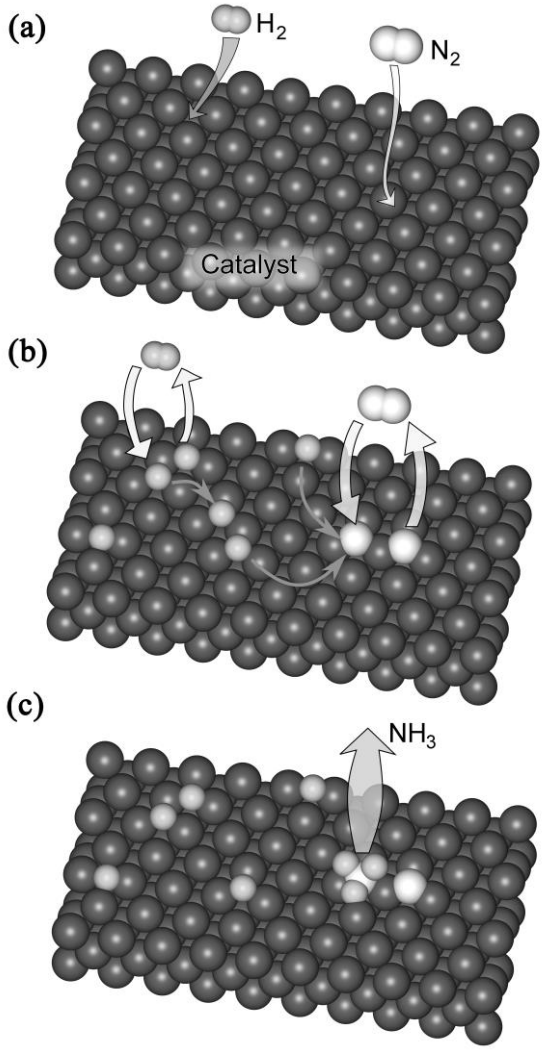

Fig. 1. Scheme of ammonia synthesis on iron catalysts. (a) Initial reaction stages of dissociative adsorption of substrate molecules, (b) formation of highly mobile hydrogen species that sequentially react with nitrogen atomic species, (c) ammonia desorption from the catalyst surface.

The H-B process has progressed in terms of energy consumption, decreasing by almost three times to 0.48 MJ per mole of ammonia produced. This improvement has been

brought about by the change of feedstock, from coal to natural gas, and improvements in the technical aspects of the process enabling all available heat to be utilised [9].

Another important issue of the modern H-B process is the requirement of the non-renewable natural gas to generate hydrogen. Considering sustainable H-B process that uses hydrogen generated by the electrolysis of water (it requires 360-480 kJ/mol [43]), the energy consumption of renewable production of ammonia by the H-B will be almost 3 times higher - 1.5 MJ/mol, which is more than the energy consumption of many other alternative methods (see section 6).

3. Plasma-Induced Nitrogen Fixation

Nitrogen fixation in plasma is one of the pioneering ways of industrial nitrogen fixation and may be subdivided into two broad areas - thermal plasma and non-thermal plasma. The equipment required, reaction mechanisms, the energy efficiency of these processes are very different, so these methods are discussed separately, in sections 3.1 and 3.2, respectively.

3.1 Thermal Plasma Nitrogen Fixation

Thermal or equilibrium plasma is partially ionised gas in which the temperature of charged particles, mainly electrons, is close to that of neutral particles, *i.e.* the system may be described in terms of thermal equilibrium with a temperature of the order of 10^3 K. The generation of thermal plasma is relatively simple and does not require sophisticated energy conversion equipment. As a result, its application in NF has been extensively studied. Thermal plasma NF, the Birkeland-Eyde process, was one of the

early approaches of industrial NF. Air flow went through an arc discharge zone followed by quenching with water and a series of adsorption stages producing about 1% of nitric oxide with the energy consumption of 3.4 – 4.1 MJ/mol HNO_3, Fig. 2 [44,45]. More recent examples of thermal plasma NF on the laboratory scale demonstrated higher energy consumption ranging from 10 to 1000 MJ/mol [46–49]. A combination of thermal plasma and catalysis was patented by O`Hare [50–52], and Amouroux and Cavadias [53] with the NF energy consumption was reported only for the second system (NiO/WO_3 catalyst) as being 4.7 MJ/mol HNO_3 [53].

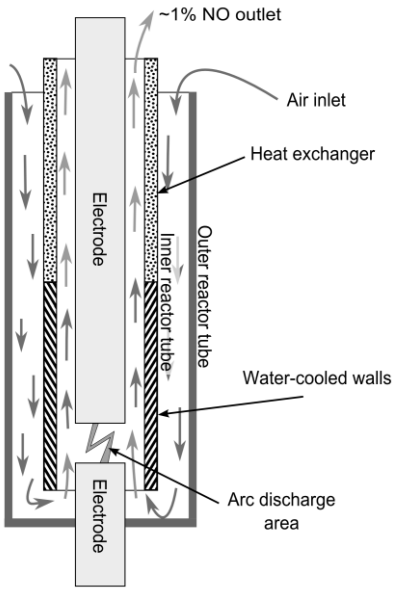

Fig. 2. Scheme of Birkeland-Eyde arc discharge apparatus [44,45].

Thermal plasma NF may be rationalised in terms of thermodynamics by considering two competing processes: (a) the formation of NO, (b) atomization of dinitrogen and dioxygen molecules [54,55]. At lower temperatures, dinitrogen and dioxygen molecules dominate, while at higher temperatures they dissociate to atoms It is only at the temperature near 3500K that the NO concentration is the highest at approximately 7%,

Fig. 3 [54]. Such a low concentration demonstrates that most of the energy is spent on gas heating rather than on dinitrogen oxidation reaction.

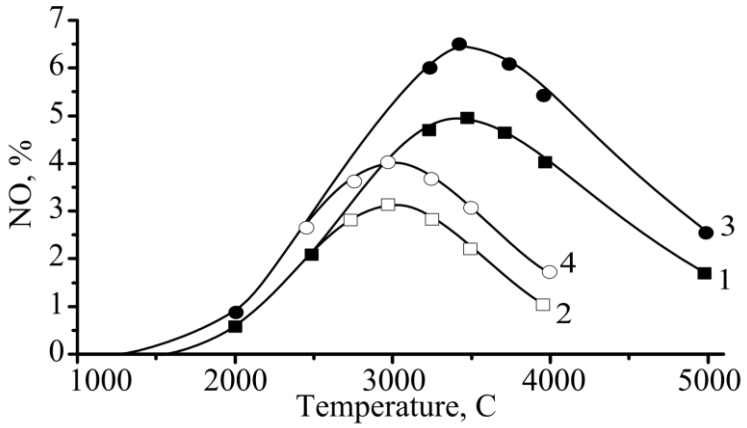

Fig. 3. Equilibrium concentrations of NO in (1) air at 10^5 Pa, (2) air at $6.6 \cdot 10^3$ Pa, (3) $N_2/O_2 = 1/1$ at 10^5 Pa, (4) $N_2/O_2 = 1/1$ at $6.6 \cdot 10^3$ Pa. Adapted with permission from ref. [54].

With respect to environmental considerations, NF with plasma looks very promising. It converts abundant air into valuable products using only electrical power. This means that by using renewable energy sources, nitrogen fertilisers can be produced with no greenhouse gas emissions, because plasma generates essentially no waste and uses no solvents. Thermal plasma, however, requires high temperatures and the energy efficiency is low. Even the theoretical energy consumption of 0.86 MJ per mole of NO produced, which may be achieved at 20-30 bars, a temperature of 3000-3500K and a fast rate of cooling, 10^7 K/s [56], is too high by current standards and because of this reason research in this method has not progressed much in recent years.

3.2 Non-thermal Plasma Nitrogen Fixation

Non-thermal or non-equilibrium plasma cannot be described in terms of a single thermal equilibrium, because electron temperature may be several orders of magnitude higher than the temperature of neutral molecules. Hence, using non-thermal plasma, it is possible to generate high-energy species that can activate dinitrogen molecules while keeping the reaction temperature and energy consumption low. In this respect, the vibrationally excited ground-state dinitrogen species (N_2^*) obtained by collisions with highly energetic electrons play the most important role, equation 1 [57–61]. Once formed, excessive energy stored in vibrational modes may be efficiently provided for chemical reactions to overcome the high activation barriers of dinitrogen reactions as in equations 1-3 [56,58,62].

$$e^- + N_2 \rightarrow e^- + N_2^* \quad (1)$$

$$O + N_2^* \rightarrow NO + N^* \quad (2)$$

$$O_2 + N^* \rightarrow NO + O \quad (3)$$

Rusanov, Fridman and Sholin outlined the experimental conditions required to achieve high energy efficiencies of NF [56]. Firstly, a large amount of vibrationally excited dinitrogen molecules should be created using non-thermal plasma with an electron temperature of at least 10^4 K. Secondly, in order to maximise the energy efficiency, the process should be performed under medium pressure, between approximately 0.1 and 130 kPa. Thirdly, the temperature of the resulting gas should not be very high, because otherwise the product formation would be described by equilibrium with low yield and low energy efficiency [56,57]. Fulfilling these criteria, Azizov *et al.* [63] performed the

oxidation of dinitrogen in microwave-induced plasma with the energy consumption of 0.29 MJ/mol, higher than that of the H-B process.

The vibrational excitation of dinitrogen molecules to decrease activation barriers may be applied not only to gas-phase reactions, but to heterogeneously catalysed reactions [58]. Catalysts can activate oxygen or hydrogen, and thereby further increase the energy efficiency of plasma NF. Many research groups have observed the catalytic effects during plasma synthesis [64–69], but Mutel *et al.* demonstrated the highest energy efficiency of dinitrogen plasma oxidation in the presence of an MoO_3 catalyst [70]. In comparison to non-catalytic plasma nitrogen fixation, the MoO_3 catalyst decreased the energy consumption of nitrogen fixation by 35% under the same conditions to 0.86 MJ/mol [70].

However, NF and plasma catalysis are not well studied and the mechanism of plasma-catalyst interaction is not clear. At a pressure of 10kPa, the mean free path of a gas molecule is about 10^{-6} m, lower than the dimensions of a catalytic reactor (~10^{-2} m). This means that when N_2* species are formed in plasma, they collides with 10^2 to 10^5 other gas-phase molecules depending on the pressure, and dissipate the energy acquired from plasma before contacting the catalyst. Taking into account the review of plasma pollution abatement by van Durme *et al.* [71], the question of plasma-catalyst interaction may be resolved by the observed enhanced formation of microscopic plasma channels near the catalyst surface or within its pores [71,72], so the distance between the site of active specie formation to the catalysts is small. On the other hand, no authors studying plasma catalytic nitrogen fixation, to the best of our knowledge, have paid attention to the fact that the most widely used catalyst (MoO_3) is relatively volatile

[73]. Under irradiation with high-energy particles in plasma, these catalysts may vaporise and act as a homogeneous gas-phase oxidation catalyst materials. In this regard, the identification of the plasma-catalyst interaction mechanism is important for the selection of the most suitable and active NF catalysts.

Therefore, NF with non-thermal plasma combines the environmental advantages of plasma NF (utilisation of available raw materials such as air and electricity and a lack of by-product formation) with higher energy efficiency. The theoretical limit of the energy consumption of dinitrogen oxidation is approximately 0.2 MJ/mol [56,57], which is more than 2.5 times lower than that of the H-B process. On the other hand, many challenges (see section 7) should be met to convert this promising method into a competitive industrial NF technology.

4. Biological Nitrogen Fixation

The first study on biological NF was reported in 1888 involving fixation in leguminous plants [74,75]. This ability was later reported for many prokaryotic organisms and symbiotic systems except eukaryotes, and extensive research is now conducted on biological NF as well as the core of the process itself, the nitrogenase enzyme. In this regard, two detailed mechanistic studies were reported by Peters and Szilagyi [76] and by Hoffman *et al*. [77].

Nitrogenase enzyme is not a single protein, but a whole family of proteins capable of catalysing the reduction of dinitrogen to ammonia. These enzymes are homologous to each other, consisting of two proteins: dinitrogenase reductase and dinitrogenase. Dinitrogenase binds and reduces dinitrogen molecules, while dinitrogenase reductase

reduces dinitrogenase protein [74]. Different nitrogenase enzymes are so similar that it is possible to take the first part (dinitrogenase reductase) from one organism and the second part (dinitrogenase) from another organism to obtain an operational nitrogenase enzyme.

The most studied nitrogenase enzyme is the Mo-dependant nitrogenase that consists of Fe-containing dinitrogenase reductase and MoFe-containing dinitrogenase, Fig. 4. There are similar proteins where molybdenum is substituted with vanadium or iron [78]. As molybdenum is very rare in the environment, some nitrogen-fixing bacteria "know" many nitrogenase enzymes and choose a particular one depending on the availability of precursor molecules [74,75].

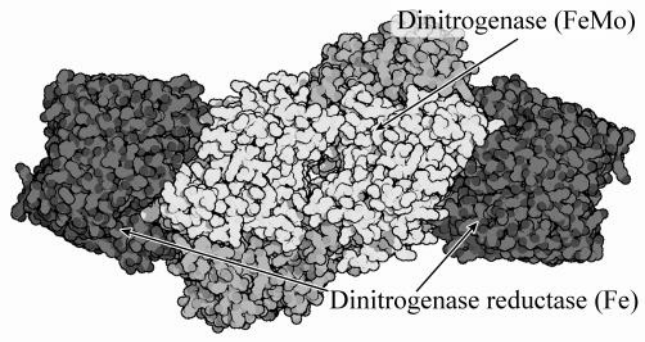

Fig. 4. Structure of the Mo-dependant Nitrogenase Enzyme (Reprinted with permission from RCSB PDB) [79].

The structure of the FeMo-protein and its effect on the reaction and mechanism has been the subject of extensive research, but it is difficult to say that the reaction mechanism is established [77,80]. However, the structure of the central unit of the

FeMo-protein was accurately described, by Einsle *et al.*,[81] although the nature of the active sites and the particular reaction stages are widely disputed. The Mo centre of the enzyme is believed to bind and reduce dinitrogen and several Mo-containing metallocomplex catalytic systems supported these assumptions acting as simple models of biological systems [8,75,82–84]. The discovery of Fe-containing complexes capable of catalytic dinitrogen reduction, however, shifted the attention to Fe centres [85].

The overall mechanistic scheme of biological nitrogenase-based nitrogen fixation is now widely accepted. The hydrolysis of adenosine triphosphate (ATP) molecules to adenosine diphosphate (ADP) transfers electrons to the dinitrogenase protein where dinitrogen molecule is stepwise reduced to ammonia. Two ATP molecules are needed for every electron transfer, so at least 16 ATP are required to fix a single N_2 molecule as in equation 4 [74,77,78].

$$N_2 + 8H^+ + 8e^- \rightarrow 2NH_3 + H_2 \quad (4)$$

Six of the eight electrons reduce dinitrogen, while the other two produce an unavoidable by-product, hydrogen, and this means that the "electron efficiency" of the process is 75%. As ATP is usually called a molecular unit of energy currency, it is reasonable to recalculate the energy consumption in biological nitrogen fixation using conventional units. The energy consumed in the hydrolysis of ATP to ADP under biological conditions was determined by Fioleta *et al.* [86] to be 55 kJ/mol and by Kammermeiner *et al*. [87], to be between 48 and 63 kJ/mol. Assuming that the same amount of energy is required for the backward reaction of ATP production from ADP, the amount of energy required to convert ½ N_2 molecule into other forms is estimated to be 0.38

MJ/mol. This number is slightly smaller than the efficiency of the H-B process (0.48 MJ/mol) [9]. More accurate estimations of the energy efficiency were performed by Alberty [88,89], who studied the apparent reduction potentials of biochemical reactions and demonstrated that the pH, ionic strength and Mg^{2+} concentration significantly affected the reduction potential. Based on these data, the Gibb's free energy of ammonia formation was estimated to be between 63.2 and 180 kJ/mol.

From an industrial perspective and accounting for energy losses in biological processes, the energy efficiency of biological fixation may also be estimated from the molecular respiratory cycle. It is widely accepted that the oxidation of a glucose molecule produces up to 36 ATP molecules. In the recent review, Rich estimates this amount to be 29.85 ATP per glucose molecule [90]. On the other hand, full oxidation of glucose under standard conditions produces 2.87 MJ/mol of energy [91], so each ATP "stores" about 96 kJ/mol of energy, so biological fixation requires approximately 0.77 MJ per mol of NH_3 produced.

It is difficult to evaluate the accuracy of these estimations, but studies suggest that the real efficiency might be lower. Burris and Roberts assume that "under natural conditions, 20 to 30 ATP molecules, rather than 16 MgATP, are needed" [74]. In addition, various types of nitrogenase enzymes have various maximum "electron" efficiency and for Mo-nitrogenase this is up to 70%, for V-nitrogenase 40%, while for Fe-nitrogenase it is only 20% [75]. These data demonstrate that the energy efficiency of biological nitrogen fixation is comparable to that of the H-B process. It is therefore not surprising that even bacteria capable of fixing atmospheric nitrogen are very "reluctant"

to exercise this ability – they do it only if there are no better suitable nitrogen sources [74].

The advantage of biological NF from an environmental point of view is that the process is self-regulating and consumes renewable and environmentally benign substances such as carbohydrates. If the natural symbiosis between crops and nitrogen-fixing bacteria is enhanced [92,93], it may lead to a decrease in the need for artificial fertilisers and the problems associated with the efficient use of fertilisers [1,4–6,94–97]. Another promising application of biological NF is the treatment of various organic wastes from agriculture or forestry [98,99], where the side-product of one process may be used as a feedstock for biological NF.

5. Metallocomplex Nitrogen Fixation

For a long time, it was believed that dinitrogen was too stable to react under mild conditions except on enzymes or metallic lithium, which formed nitrides when contacted with dinitrogen at room temperature. A major breakthrough was achieved when Vol'pin and Shur reported in 1964 the first organic reaction of N_2 molecule – the reduction with dicyclopentadienyltitanium chloride and ethylmagnesium bromide in ether [100]. In the following year, the first dinitrogen complex of transition metal, $[Ru(NH_3)_5(N_2)]^{2+}$, was obtained by Allen and Senoff from a hydrazine solution [101]. During the following decades, many non-catalytic reaction routes for the conversion of dinitrogen molecules into dinitrogen complexes were reported and there were some important metallocomplex NF catalytic cycles that form either organic and silicon-

organic compounds or ammonia [75,102–104] and these systems can be considered as promising routes to industrial NF.

Shiina has reported that chlorides of transition metals dissolved in THF acted as homogenous catalysts for the silylation of N_2 under ambient conditions [105], Fig. 5a. A yield to catalyst ratio of 5.4 was obtained for $CrCl_3$ catalyst, while no silyamine formation took place without the catalyst. Similar reactions were reported for milder reducing agents (Na), but with more complex catalysts such as $[Mo(N_2)_2(PMe_2Ph)_4]$ [106,107]. These catalysts have been significantly enhanced, producing up to 226 silyamine molecules per catalyst molecule [7], Fig. 5b. On the other hand, Mori employed metallic Li as a reducing agent and several Ti-based homogenous catalysts to introduce various N-containing functional groups to certain organic molecules using gaseous nitrogen, obtaining product yields between 250 and 350% (based on the amount of the catalyst) [108].

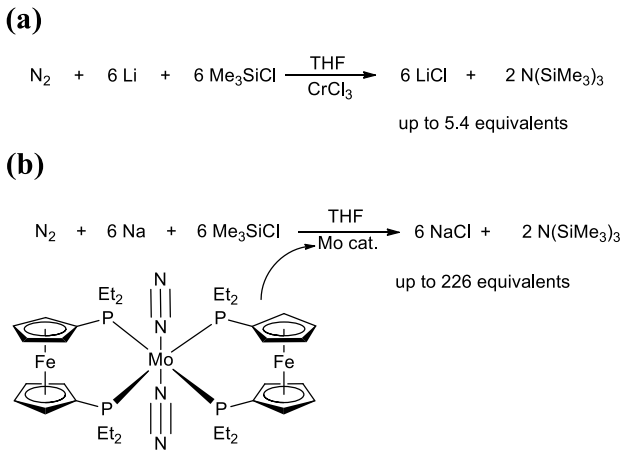

Fig. 5. Silyamine production from dinitrogen. (a) Pioneering process proposed by Shiima[105] using $CrCl_3$ catalyst in THF. (b) Recent, Mo-catalysed enhanced system proposed by Tanabe *et al.*[7]. Product yields are based on the catalyst.

Several catalytic systems are known to produce simple nitrogen compounds such as ammonia or hydrazine. In the 1980s, Shilov proposed a Mo-containing system, which catalysed the conversion of dinitrogen to a mixture of ammonia and hydrazine (NH_3 to N_2H_4 in a ratio of 1:10-100), Fig. 6a. [8,75,82]. The catalyst optimised was a polynuclear complex obtained in a methanol solution from $MoCl_5$ in the presence of $MgCl_2$, Fig. 6b. This complex used sodium amalgam as a reducing agent and catalysed the reduction of up to 10^3 dinitrogen molecules at ambient pressure and up to 10^4 at 7 MPa of N_2 [82].

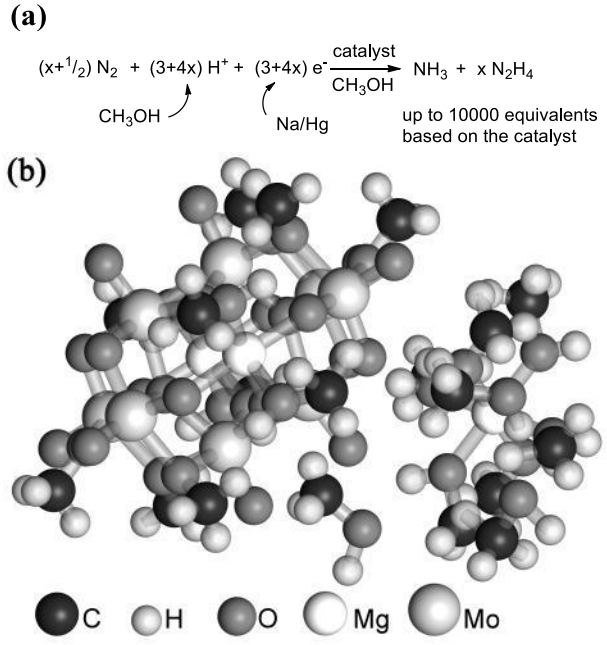

Fig. 6. Dinitrogen reduction scheme proposed by Shilov. (a) Reaction scheme of the reaction on $\{[Mg_2Mo_8O_{22}(MeO)_6(MeOH)_4]^{2-}[Mg(Me(OH)_6]^{2+}\}\cdot 6MeOH$ catalyst. (b) Crystal structure of the catalyst [109,110].

Yandulov and Schrock [84], proposed a Mo-containing homogenous catalytic system capable of reducing dinitrogen to ammonia at ambient conditions. The reaction took place in a hexane solution with {LutH}{BAr*$_4$} as a proton source and decamethylchromocene as a reducing agent, Fig. 7. The Mo-containing catalyst produced 7.5 to 8 equivalents of NH_3 with a yield of 65%, which is smaller than the optimal efficiency of Mo-dependant nitrogenase (~75%). In order to obtain such high yields, however, the reaction rate was decreased by slow addition of the reducing agent and by using hexane, a solvent in which the reacting compounds had limited solubility [84]. Following the discovery of this reaction, a lot of effort was made to investigate the nature of the intermediate states [111], the use of other ligands [112], the parallels between this reaction and the action of the nitrogenase enzyme [113], but no major improvements in catalyst efficiency were archived.

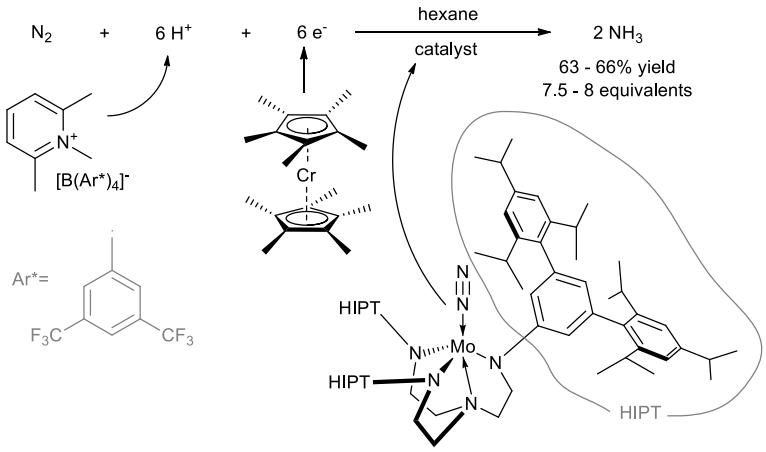

Fig. 7. Homogeneous metallocomplex catalytic system for dinitrogen reduction proposed by Yandulov and Schrock [84].

Recently, Arashiba *et al.* [83], proposed a Mo complex with PNP-type pincer ligands capable of reducing gaseous dinitrogen to ammonia. Cobaltocene [$Co(C_5H_5)_2$] was used as a reducing agent and [LutH]OTf as a proton source producing up to 12 equivalents of ammonia from 1 equivalent of the catalyst, Fig. 8.

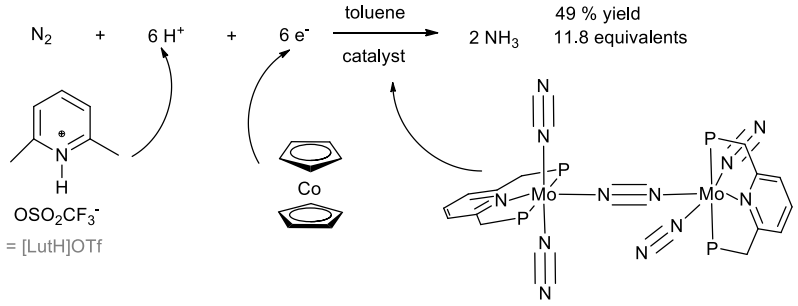

Fig. 8. Homogeneous metallocomplex catalytic system for dinitrogen reduction proposed by Arashiba *et al.*[83].

Similar results were obtained when a stronger reducing agent, decamethylchromocene [$Co(C_5(CH_3)_5)_2$], was used. In this reaction, a proton source had to be carefully selected because highly acidic compounds directly protonated the catalyst and a proton source with highly coordinating counter anions displaced ligands around the Mo atom decomposing the catalyst and thereby reducing the reaction yield [83]. Anderson *et al.* proposed an Fe-based catalytic system that demonstrated that Fe sites of nitrogenase enzyme may be responsible for dinitrogen binding, Fig. 9 [85].

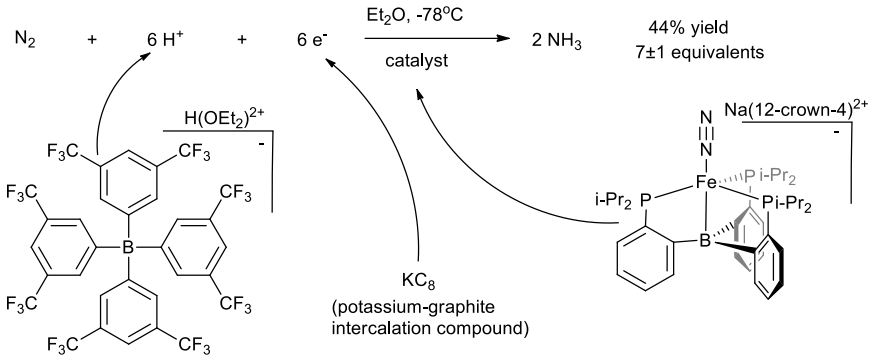

Fig. 9. Homogeneous metallocomplex catalytic system for dinitrogen reduction proposed by Anderson *et al.* [85].

Nitrogen fixation using metallorganic complexes is still very far from large-scale applications due to low yields, fast catalyst decomposition and extremely expensive compounds (reducing agents, proton source compounds used in stoichiometric quantities as well as catalyst materials). However, the approach proposed by Shilov combines the largest product to catalyst ratio (up to 10^4) with ease of estimations of the energy efficiency, Fig. 5a [82]. It is possible to perform a lower-boundary estimation of the energy efficiency assuming that the recycling of sodium (*i.e.* converting sodium methoxide to metallic sodium) is the only energy-demanding step. In order to estimate the energy consumption of this process, the production of metallic lithium may be considered because it uses the same techniques (electrolysis of melted salts) and experimental data on this process is readily available. The energy consumption of NF with metallic lithium may be estimated using the information provided in Table 1, as 2.73 MJ per ½ N_2 mole [114]. The same number may be used as a lower-boundary estimation of the energy consumption in metallocomplex NF with the catalysts proposed by Shilov [82] or similar systems that use alkaline metals as reducing agents.

Table 1 Nitrogen Fixation Cycle with Metallic Lithium

Fixation with Li			SN[a]
$6Li + N_2$	→	$2Li_3N$	1
$Li_3N + 3H_2O$	→	$3LiOH + NH_3$	2
$LiOH + HCl$	→	$LiCl + H_2O$	6
$LiCl$	→	$Li + ½\ Cl_2$	6
$N_2 + 6HCl$	→	$2\ NH_3 + 3\ Cl_2$	

[a] Stoichiometric number

The disadvantage of metallocomplex nitrogen fixation is the complexity of the reactions, the stoichiometric yields and excessive use of solvents. Metallocomplex NF resembles the pharmaceutical industry in its complexity with an E-factor (mass of waste per unit of mass of product) estimated at 25-100 [115]. The use of ambient pressure seems to be an important advantage that implies low energy consumption. However, metallocomplex NF requires more than 5 times as much energy to fix $½N_2$ molecule as the H-B process, 2.7 MJ/mol compared to 0.48 MJ/mol [9]. Considering all of these factors, the most important advantage of metallocomplex NF is the possibility to study reaction mechanisms and parallels between biological processes [116] rather than from the perspectives for large-scale industrial NF in the near future.

6. Conclusion

At the beginning of the 20th century, the H-B process has been a major step forward in terms of green chemistry, producing needed nitrogen fertilizers from atmospheric nitrogen at a low price and enabling previously used non-renewable mineral fertilisers to be fully substituted by fertilisers produced from atmospheric nitrogen [115]. Ru-based catalysts provide higher activity and lower pressure, but they deactivate easily and are more expensive thus hindering the replacement of existing catalysts with Ru-based systems. Although novel nitride catalysts, such as Co_3Mo_3N, demonstrate high activity and deactivation stability, iron-based catalysts are still the default choice for industry. In terms of energy efficiency, the H-B process is most efficient process than the other industrial methods, and it has a lower power consumption in comparison to the theoretical limit of thermal plasma NF. However, to the energy efficiency of the H-B is very close to its theoretical limits and modern ecological standards require a further reduction in its environmental footprint.

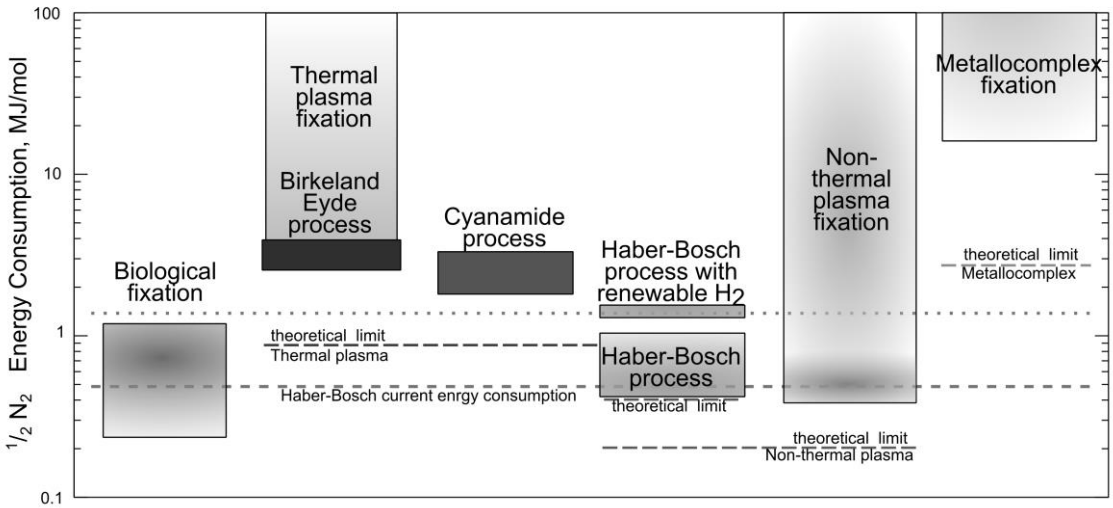

Fig. 10. Comparison of the energy consumption of NF. The H-B process has the lowest consumption, but now it is close to its theoretical limits. Among other alternatives only non-thermal plasma NF demonstrates high efficiency and has very low theoretical limit of power consumption.

Biological NF is a typical example that shows the inefficiency of the industrial processes, because NF in nature takes place unnoticeably at ambient temperature and pressure, while industrial ammonia synthesis requires tons of natural gas to be burned and thick-walled steel reactors to contain high pressure. However, our estimations suggest that this picture is rather misleading because the energy consumption of biological NF and the H-B process are comparable (Fig. 10). From an environmental viewpoint, biological NF has a lot of promise because it is a self-regulating process that has no environmental problems associated with the introduction of artificial fertilisers [4–6,94]. Full utilisation of biological NF in combination with artificial fertilisers where possible may considerably decrease the environmental footprint of industrial nitrogen fixation and mitigate the problems associated with fertiliser overuse.

Metallocomplex NF, an artificial analogy of biological NF, appears particularly promising as dinitrogen molecules are converted into valuable nitrogen compounds under ambient temperature and pressure. At the current stage of metallocomplex NF method development, NF yields are low, the chemicals required for synthesis are complex and expensive and these systems are still far from industrial applications.

With respect to the future developments in NF, non-thermal plasma seems to be the only promising method because thermodynamic limitations associated with the process may be bypassed by directing the energy into one particular reaction pathway. With respect to NF in non-thermal plasma the highest NF energy efficiency is expected when vibrationally excited the dinitrogen molecules are formed in sufficient quantities, the temperature of the resulting gases is not very high to decompose the reaction products and the reaction is channelled to a particular reaction pathway. Non-thermal plasma NF has many environmental advantages as it requires only electricity and air as a feedstock and the process takes place under ambient pressure. This means that instead of large scale high-pressure ammonia synthesis plants, plasma NF may be performed on a much smaller scale, producing the fertilisers where they are needed, eliminating the problems associated with transportation and the storage of fertilisers.

7. Challenges

It is clear from this review that many technical and scientific challenges remain with the NF processes despite the strides that have been made in understanding nitrogen fixation by organisms and the approaches that are adopted on an industrial scale. Although biological NF cannot be directly applied to industry, it is particularly important to mention because biological and industrial NF occur side-by-side - artificial fertilisers are important in intensive agriculture, while extensive agriculture practised in developing countries relies primarily on biologically-fixed nitrogen. Thus, wider application and enhancement of biological NF, for example by means of genetic

engineering of traditional crops, may significantly affect developing countries, improving the crops and decreasing the need for artificial fertilizers [93,95–97].

The H-B process may remain the most important way of NF for many decades, but it is a very energy-demanding industrial process that is very close to technological limits leaving almost no room for further improvement by process optimisation. Further development in economic and environmental terms requires addressing the two main challenges of increasing the energy efficiency and utilizing renewable feedstock and raw materials. These challenges can be met by the development of renewable hydrogen production methods, for example, using photocatalytic water splitting [117,118]. Also the development of novel, more active catalysts is essential, the catalysts that can reduce the activation energy of dinitrogen dissociative adsorption and decrease the reaction temperature to about 470 K and thereby increase ammonia yield by 4-5 times at the same operation pressure. The last century of catalyst screening of more than 100`000 catalysts [12] has demonstrated that progress in the H-B process could be limited; although recent studies show that nitride based catalytic systems hold some promise [35,37,38,119].

Non-thermal plasma NF is an environmentally benign method of NF because it requires only air and electricity to generate high-value nitrogen compounds [120,121]. Industrial application of this method is however a long way away because the challenges of catalysis, technology and reaction engineering would need to be addressed.

With respect to plasma catalysts, comparative data on the activity of various catalysts in NF and the mechanism of plasma-catalyst interaction are unavailable. Further research,

including plasma catalyst screening, is essential. Another main obstacle in achieving high energy efficient NF is the high losses during energy conversion, for example, the efficiency of electrical energy conversion into microwave energy (usually 2450 MHz) is just 40-65% [122]. In addition to catalyst selection and design, there is the challenge of reactor engineering that should integrate the developments of plasma catalysis and optimise the product output and the energy efficiency of the process to create an efficient and suitable plasma reactor for the end user.

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